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# Urea and deuterium mixtures at high pressures

M. Donnelly,<sup>1,a)</sup> C. L. Bull,<sup>2</sup> R. J. Husband,<sup>1</sup> A. D. Frantzana,<sup>1</sup> S. Klotz,<sup>3</sup> and J. S. Loveday<sup>1</sup>

<sup>1</sup>Centre for Science at Extreme Conditions and School of Physics and Astronomy, The University of Edinburgh, Erskine Williamson Building, Peter Guthrie Tait Road, The King's Buildings, Edinburgh EH9 3FD, United Kingdom

<sup>2</sup>ISIS, Rutherford Appleton Laboratory, Oxford Harwell, Didcot OX11 0QX, United Kingdom

<sup>3</sup>IMPMC, CNRS UMR 7590, Université P & M Curie, 4 Place Jussieu, 75252 Paris, France

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Urea, like many network forming compounds, has long been known to form inclusion (guest-host) compounds. Unlike other network formers like water, urea is not known to form such inclusion compounds with simple molecules like hydrogen. Such compounds if they existed would be of interest both for the fundamental insight they provide into molecular bonding and as potential gas storage systems. Urea has been proposed as a potential hydrogen storage material [T. A. Strobel *et al.*, Chem. Phys. Lett. **478**, 97 (2009)]. Here, we report the results of high-pressure neutron diffraction studies of urea and D<sub>2</sub> mixtures that indicate no inclusion compound forms up to 3.7 GPa. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4915523>]

## I. INTRODUCTION

Inclusion or guest-host compounds are an important and interesting group of materials. They consist of a network forming host which contains voids or channels which are capable of incorporating a guest species.<sup>1</sup> The presence of the guest obviously has strong effects on the host, and its bonding and inclusion compounds often access network configurations not adopted by the network former alone. For example, the clathrate hydrate structures are not adopted by water in the absence of a host and hence have no stable ice analogues.<sup>1</sup> Inclusion compounds also have wide applications as storage and filter systems. Under appropriate conditions, they can incorporate significant amounts of guest and by a change of thermodynamic conditions can be induced to release unchanged guest molecules.<sup>2</sup> Often the conditions required to produce a particular inclusion compound can be used to separate different guest species. For example, the proposed use of carbon dioxide hydrates to remove carbon dioxide from flue gas.<sup>3</sup>

Whilst network formers like silica, water, and metal organic framework compounds have been very widely studied for their ability to take up guest species, urea, a simple hydrogen bonded organic network former has been less widely studied. It is known to form inclusion compounds with long-chain hydrocarbons<sup>4,5</sup> but currently, little is known about its ability to take up simple gases (for example, methane, hydrogen, and nitrogen) all of which form several different inclusion structures when mixed with water. Urea however is a potentially valuable inclusion compound former. It is readily available in nature as a major component of *Avian Stercore* and hence is cheap. It is relatively environmentally benign and is widely used as a deicer in situations where rock-salt cannot be used. Finally, its structure at ambient pressure which is tetragonal (space group  $P-42_1m$ ,  $a = b = 5.589$  Å,  $c = 4.680$  Å) has square channels

formed from hydrogen bonded planar urea molecules running along the tetragonal  $c$ -axis (see Figure 1). These channels, which are 5.6 Å across, are large enough to accommodate a simple molecule.<sup>6–8</sup> Furthermore, neutron and x-ray diffraction studies of pure urea have identified three high-pressure phases at room temperature.<sup>6–8</sup> The ambient pressure form transforms to an orthorhombic structure above 0.5 GPa known as phase III ( $P2_12_12_1$ ,  $a = 8.272$  Å,  $b = 3.624$  Å,  $c = 8.844$  Å). At around 2.8 GPa, phase III of urea transforms to another orthorhombic structure known as phase IV ( $P2_12_12$ ,  $a = 3.414$  Å,  $b = 7.360$  Å,  $c = 4.606$  Å) and then transforms above 7.2 GPa into a further orthorhombic phase V ( $Pmcn$ ). These transformations indicate that pressure has strong effects on the network bonding and thus may access new inclusion compounds.

Similarly, hydrogen is a good guest species as it is the smallest diatomic gas and diffuses readily through most liquids and solids. It readily forms inclusion compounds with water and to date four different hydrate structures have been identified at different pressures and temperatures with a fifth predicted but not yet confirmed experimentally.<sup>9–11</sup> Hydrogen inclusion compounds have the added technological benefit that if their hydrogen content is high enough, they may form the basis of a hydrogen storage system.<sup>12</sup> Such a storage system is one of the principal hurdles to be overcome in the development of hydrogen based energy economy. Hydrogen-urea has been suggested as such a potential system.<sup>12</sup> However, to date, there have been no searches for hydrogen-urea inclusion compounds. In this paper, we present the first results from neutron diffraction experiments on mixtures of urea and deuterium<sup>13</sup> at high pressures. Our results suggest that urea does not form clathrates with deuterium within the pressure and temperature range studied.

## II. EXPERIMENT

Below 0.3 GPa, an aluminium gas cell was used with a preformed Bridgeman seal for the neutron diffraction studies

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: m.donnelly-2@sms.ed.ac.uk.

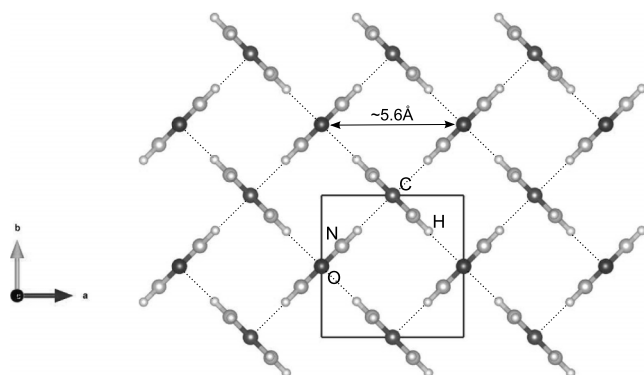


FIG. 1. The crystal structure of the tetragonal phase I of urea ( $P-42_1m$ ) showing the channels running along the  $c$  direction. Dotted lines mark the hydrogen bonds between the urea molecules.

of urea and deuterium. Powdered deuterated urea was placed in the gas cell. The cell was then pressurised using  $D_2$  gas; the pressure of which was carefully controlled by an in-house control panel and Hi-Pro capstan 0.3 GPa pump suitable for use with deuterium. The gas cell was mounted on the PEARL instrument at the ISIS neutron facility, UK. Time-of-flight (t-o-f) diffraction data were collected in  $90^\circ$  scattering geometry at room temperature at a series of gas pressures up to 0.3 GPa.

For the higher pressure neutron diffraction experiments above 0.3 GPa, a Paris-Edinburgh (PE) press was used to generate pressure on a mixture of deuterium and urea. Powdered urea was placed in a deuterium-proof encapsulated copper beryllium gasket (modified from the standard titanium-zirconium alloy encapsulated gasket<sup>8</sup>) between a pair of standard tungsten-carbide anvils with a toroidal profile.<sup>14</sup> The anvils are part of a specially designed clamp that allows high-density gases to be loaded into the sample chamber formed by the gasket assembly and then sealed by the application of load to the anvils. The clamp is placed in a specialised deuterium gas loading pressure vessel and charged with 0.2 GPa of  $D_2$  gas. The clamp is then sealed so as to retain the high density  $D_2$  gas in the sample volume. This process has been fully described elsewhere.<sup>15</sup> The sealed clamp is then placed in a VX3 variant Paris-Edinburgh press<sup>16</sup> and mounted on the PEARL instrument. Diffraction patterns were obtained in the

$90^\circ$  scattering geometry with increasing applied hydraulic load to increase the sample pressure. Each diffraction pattern was collected over approximately 3–4 h.

For both experiments, data were reduced using the Mantid software suite<sup>17</sup> and the resulting diffraction patterns were analysed by Rietveld profile refinement using the GSAS software suite.<sup>18</sup> Although the data were analysed by Rietveld refinement, the relatively small proportion of urea in the sample volume that was necessary for the deuterium loading procedure resulted in a low signal level which prevented refinement of the atomic fractional co-ordinates.

### III. RESULTS

Figure 2(a) shows a neutron diffraction pattern of the as-loaded deuterated urea sample at 293 K in the aluminium gas cell. The diffraction peaks can be assigned to the known tetragonal phase I of urea and the aluminium of the gas cell. To check whether there is any filling of the voids of the urea structures by deuterium, the lattice parameters of the unit cell can be followed as a function of pressure. If there were some inclusion of the  $D_2$  into the structure, this would be expected to be manifested in anomalies in the lattice parameters and changes in the relative intensities of the reflections.

Upon pressurisation of the sample with  $D_2$  gas, the reflections move to lower d-spacing as expected with increasing pressure as shown in Figure 2. The refined lattice parameters as determined by Rietveld analysis of the patterns shown in Figure 2(a) are shown in Figure 2(b). No anomalies are observed in the unit cell parameters on compression suggesting that no deuterium has entered the phase I structure and that normal compression behaviour of the sample is being observed. Based on the gas cell data, the bulk modulus of the sample in the range 0–0.3 GPa was determined to be 10.4(2) GPa using a Murnaghan equation of state.<sup>19</sup> At pressures up to 0.3 GPa, the diffraction patterns can all be fitted by the known structure of tetragonal phase I of urea, and there is no obvious transition to a new inclusion phase.

At pressures above 0.3 GPa, the Paris-Edinburgh press was used to compress a mixture of deuterium and deuterated urea. A neutron diffraction pattern of the as-loaded sample

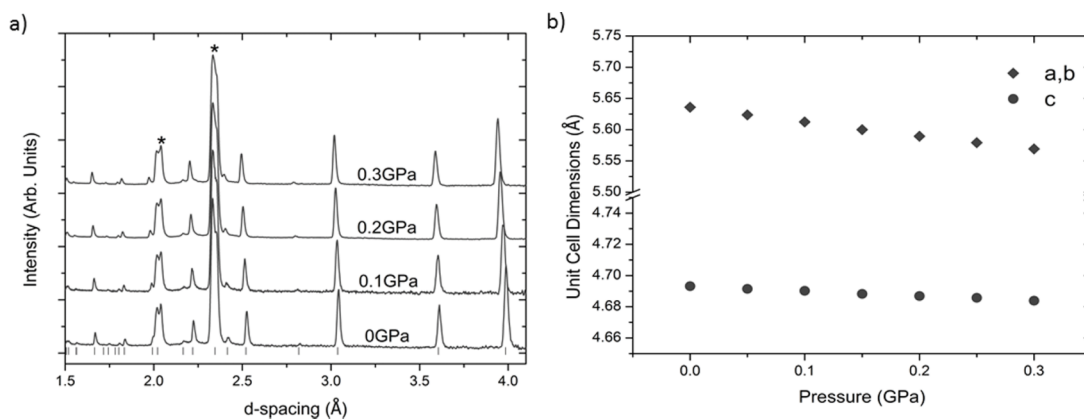


FIG. 2. The neutron diffraction patterns of urea compressed with  $D_2$  gas and the refined unit cell parameters as a function of pressure below 0.3 GPa. Figure (a) shows the diffraction patterns from urea compressed with  $D_2$  gas between 0 and 0.3 GPa. Asterisks mark contaminant reflections from the gas cell and the ticks mark reflections from the tetragonal phase I of urea. Figure (b) shows the lattice parameters obtained from Rietveld refinement of phase I of urea to the diffraction patterns shown in (a).

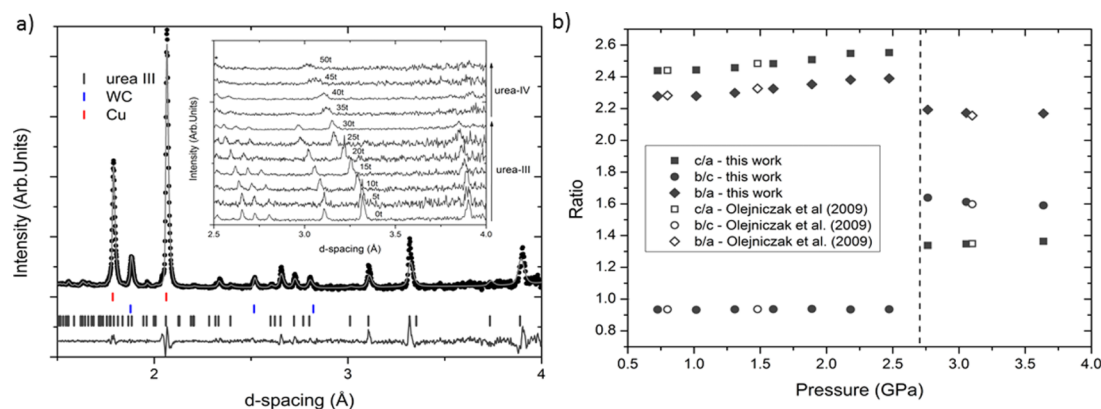


FIG. 3. Neutron diffraction data and refined unit cell parameters of urea and  $D_2$  at pressures above 0.3 GPa. Figure (a) shows a Rietveld refinement of the urea phase III structure to the profile of the as-loaded urea sample. The inset shows diffraction patterns at increasing load applied to the Paris-Edinburgh press showing the transition from phase III to phase IV of urea. The top tick marks mark the position of reflections from copper (the gasket), the middle from tungsten carbide (the anvils), and the bottom ticks show the positions of reflections of urea III. Figure (b) shows the ratios of the unit cell parameters obtained from Rietveld refinements of the diffraction data shown in the inset of (a). Squares, circles, and diamonds show the  $c/a$ ,  $b/c$ , and  $b/a$  ratios, respectively, and the filled symbols show the data from this study while the open symbols represent data measured by Olejniczak *et al.*<sup>7</sup> The dotted line at approximately 2.75 GPa marks the phase boundary between the orthorhombic phase III ( $P2_12_12_1$ ) and the orthorhombic phase IV ( $P2_12_12$ ) of urea. Estimated uncertainties were smaller than symbol sizes and so have not been included.

(with no load applied on the PE press) is shown in Figure 3(a). Rietveld refinements (Figure 3(a)) of these data showed that all peaks can be explained by orthorhombic urea phase-III, or the gasket and anvil material surrounding the sample and that the sample pressure (all pressures above 0.3 GPa were determined by comparison of the unit cell volumes of the urea from our Rietveld refinements with those found by a previous study by Olejniczak *et al.*<sup>7</sup>) was 0.8 GPa. This high pressure of the as-loaded sample is a result of the load applied to the clamp that is required to seal the  $D_2$  gas into the sample chamber combined with the 0.2 GPa pressure at which the gas was loaded. The pressure of 0.8 GPa is quite high given the relatively small applied load of 12 tonnes. This provides a clear indication that a full charge of deuterium had been sealed. The amount of urea loaded into the sample chamber filled less than half of the available volume and so had no gas been loaded when the clamp was sealed, the pressure would have been close to ambient. Furthermore as the load was increased, the pressure rose at a rate that indicated the sample chamber was filled. And, in phase III, there is no evidence of peak broadening indicating that the sample is under near-hydrostatic conditions. Experience suggests that urea peaks broaden considerably without a hydrostatic medium such as deuterium.<sup>6</sup> These observations are important because they confirm indirectly the presence of deuterium which is a fluid at these pressures and temperatures and so cannot be observed directly in the diffraction signal. The pressure dependence of the axial ratios ( $c/a$ ,  $b/a$ ,  $b/c$ ) are shown in Figure 3(b). At an applied load of 35 tonnes (Figure 3(a) inset), corresponding to a sample pressure of approximately 2.75 GPa, a clear change in the diffraction pattern was observed. The diffraction peaks from the sample can be indexed as the orthorhombic phase IV of urea and this can be seen from the change in the axial ratios in Figure 3(b). Up to the maximum pressure of almost 4 GPa, no evidence was found of any peaks which could not be explained by either a known phase of urea or the gasket (beryllium copper) or anvil (tungsten carbide with nickel binder) materials.

The ratios of the refined lattice parameters ( $c/a$ ,  $b/a$ ,  $b/c$ ) are shown as a function of pressure alongside data from a previous x-ray diffraction study on pure urea by Olejniczak *et al.*<sup>7</sup> in Figure 3(b). Although we have used the unit cell volume to determine the pressure, it is extremely unlikely that formation of an inclusion compound would give a unit cell whose shape and size were identical to those of pure urea. Hence, the fact that the unit cell shapes (the  $c/a$ ,  $b/a$ ,  $b/c$  ratios) shown in Figure 3(b) are the same as those of pure urea<sup>7</sup> for a given pressure (or unit cell volume) indicates that there is no measureable deuterium uptake in the pressure range studied.

Thus, the behaviour of the urea sample conforms to that reported for pure urea.<sup>6–8</sup> No evidence is seen of any new phases in the diffraction signal and all transitions occur at the expected unit cell volumes and hence pressures as the transition pressures found for pure urea.<sup>6–8</sup> Furthermore, the axial ratios of the various unit cells are again within error of those observed in pure urea for the same unit cell volume (or pressure).<sup>7</sup> The absence of any new unexplained phase, or anomalies in the transition pressures and unit cell dimensions of the high pressure phases, indicates that there is no incorporation of deuterium into the urea lattice and that urea-deuterium clathrates do not form. This conclusion has been reached on the basis of experiments carried out with solid urea at room temperature. It might appear that formation of inclusion compounds under these conditions is kinetically inhibited because deuterium is unable to enter the bulk material. However, deuterium is found to be extremely diffusive at high pressure and will penetrate solid metals,<sup>20</sup> and even diamond. For this reason, it appears that the absence of inclusion compound formation we report here represents the true thermodynamic behaviour.

#### IV. CONCLUSIONS

We have investigated the possibility of forming a urea-deuterium gas clathrate at high pressure as previously suggested.<sup>7</sup> However, our high-pressure neutron-diffraction exper-



iments from 0 GPa to above 3 GPa show only compression behaviour as expected from the pure urea phases and no anomalies are observed in the lattice parameters with increasing hydrostatic pressure. This suggests that at room temperature, urea does not form any inclusion compounds with deuterium and is not a candidate for a hydrogen storage material.

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